

**REMARKS/ARGUMENTS**

Claims 1-25 are pending in the present application. Claims 5, 6, 9, 14 and 17 have been acknowledged as allowable. Claims 1 and 11 have been amended. A proposed drawing correction to FIG. 1 is attached hereto. No new matter has been introduced thereby. Upon entry of the present amendment, claims 1-25 stand ready for further consideration.

With respect to Claims 18-25 and FIG. 4, the extremely rich inlet turbogenerator 400 shown in FIG. 4 is one possible embodiment of the engine 30 (that is, the turbogenerator system 400 is plugged into FIG. 1 as engine 30). The original application discloses, for example at pages 4-5, lines 31 to line 7, various engines and oxygen enrichment devices for providing an oxygen rich stream to the engine intake. The FIG. 4 shows broken lines between the turbogenerator and the heat exchanger 57 for simplification. The water shift device 60, SOFC 40, exhaust catalyst 90, etc. of FIG. 1 are not repeated in FIG. 4 but rather are understood as being located in the area indicated by the broken lines. The rich inlet turbogenerator 400 is an alternate embodiment of engine 30 for producing a hydrogen rich engine exhaust which is used to fuel the SOFC 40 (that is, turbogenerator 400 is plugged into FIG. 1 as engine 30). The hydrogen rich exhaust produced by turbogenerator 400 is not fed only through a heat exchanger 57.

Similarly, alternate embodiments for the engine 30 in FIG. 1 are shown in FIG. 1 wherein engine 30 is a reformer, a gas generator/ an energy conversion device, or a homogenous charge compression ignition (HCCI) engine, shown in FIG. 2 (free piston gas generator 200) and shown in FIG. 3 (rich internal combustion engine system with oxygen enrichment 300).

FIGS. 5 and 7 illustrate alternate embodiments for the oxygen enrichment devices which may be employed to enhance production of hydrogen rich exhaust 50 by the

various engine embodiments plugged in at numeral 30 of FIG. 1 (e.g., engine 200 of FIG. 2, engine 300 of FIG. 3). The oxygen enrichment devices 302 (FIG. 3), 500 (FIG. 5) and 600 (FIG. 6) may be utilized as part of the various engine embodiments in the manner illustrated in FIG. 3. See the present application at page 12, lines 3-10, for example.

In embodiments, one or a combination of rich combustion devices, oxygen enrichment, etc., comprise the engine 30. For example, a homogenous charge compression ignition (HCCI) engine is used to enable extremely rich combustion. That is, the various engines plugged in at numeral 30 of FIG. 1 comprise one or a combination of rich combustion devices such as HCCI, oxygen enrichment, etc., (See, for example, the application at page 5, line 1, page 10, lines 17-26, page 16, lines 18-24, and page 17, line 30 through page 18, line 1). For example, a free piston gas generator (FIG. 2) may include super rich HCCI (See the application at page 10, lines 4-7 and lines 16-26.) The rich internal combustion engine cylinder system 300 (FIG. 3) optionally used HCCI. (See the application at page 11, lines 1-3.)

### **IN THE DRAWINGS**

The specification has been amended to correct certain typographical errors or informalities noted by the Examiner. A proposed drawing correction to FIG. 1 is enclosed correcting reference to engine 30 to include as one possible embodiment of engine 30 a homogenous charge compression ignition (HCCI) engine. See, for example, the present application at page 10, lines 23-26, page 10, lines 1-7 and 16-13, page 11, lines 1-3, page 2, etc.

### **REJECTIONS UNDER 35 U.S.C. §102 and 35 U.S.C. §103**

The Examiner has rejected Claims 1, 7, 12 and 15 under 35 U.S.C. 102(b) as being anticipated by U.S. Patent 5,727,385 to Hepburn (hereinafter "Hepburn"). Claims

1, 4, 7, 8, 10, 15 and 16 have been rejected under 35 U.S.C. 102(b) as being anticipated by U.S. Patent 3,040,519 to Rae (hereinafter "Rae). Claims 1, 7, 12, and 15 have been rejected under 35 U.S.C. 102(b) as being anticipated by U.S. Patent 4,041,910 to Houseman. Claims 2 and 3 have been rejected under 35 U.S.C. 103(a) as being unpatentable over U.S. Patent 4,041,910 to Houseman in view of U.S. Patent 3,982,910 to Houseman. Claim 13 has been rejected under 35 U.S.C. 103(a) as being unpatentable in view of U.S. Patent 5,727,385 to Hepburn. Reconsideration is respectfully requested of these rejections based upon the following considerations.

With respect to the rejection based upon Hepburn, Applicants note that Hepburn does not teach a substantially continuous optimized hydrogen rich engine exhaust as presently disclosed and claimed where the hydrogen content of the engine exhaust is optimized (increased) to generate a very high hydrogen yield. Hepburn discloses a cold start emission control comprising an exhaust gas ignition (EGI) system wherein the engine is operated in a fuel rich condition (A/F 8:1 to 11:1) to produce what Hepburn terms a hydrogen rich exhaust gas composition for a short period of time during start up. After light-off of the rear catalyst brick is achieved, normal engine operation is resumed.

While the exhaust gas composition produced with the EGI system of Hepburn is richer in hydrogen content than that produced during the engine's usual lean burn operation, the short pulse of rich fueling disclosed in Hepburn is not very rich (about 20 to 30% of the fuel hydrogen content is converted to hydrogen gas). Hepburn teaches an A/F ratio of 8:1 to 11:1, which corresponds to an exhaust gas hydrogen gas content of about 8% to about 16%. Thus, the lean burn engine of Hepburn is operated somewhat richer than lean for a short time during start-up as a temporary cold start emission control strategy. (See Hepburn at Column 5, lines 52-67.)

With respect to the rejection based upon Rae, Applicants note that Rae is a non-analogous art reference in that it is concerned with non-air breathing engines (see Rae at

Column 1). The patent of Rae does not teach or suggest an extended rich mode engine having an intake and an exhaust, said extended rich mode engine configured to operate extremely rich of stoichiometric to produce a substantially continuous optimized hydrogen rich engine exhaust as presently disclosed and claim where the hydrogen content of the engine exhaust is optimized (increased) to generate a very high hydrogen yield. See, for example, the present application at page 9, line 7, page 10, line 19, page 11, lines 14-16, page 12, lines 3-10, and page 13, line 12.

With respect to the rejection based upon Houseman, neither Houseman reference teaches or suggest an extended rich mode engine configured to operate extremely rich of stoichiometric to produce a substantially continuous optimized hydrogen rich engine exhaust as presently disclosed and claimed where the hydrogen content of the engine exhaust is optimized (increased) to generate a very high hydrogen yield. Houseman discloses an arrangement for an internal combustion engine in which one or more of the cylinders of the engine are used for generating hydrogen rich gases from hydrocarbon fuels, which gases are then mixed with air and injected into the remaining cylinders in the same engine to be used as fuel. (See Abstract of Houseman 1910.) Houseman teaches a conventional engine with, for example, 6 cylinders, one or two of which are run somewhat "rich" and the others lean. A conventional engine is limited on how rich combustion can really be. The ratio of mass loads is fixed by the number of cylinders and the speed of the engine is coupled to torque.

Houseman teaches mixing a hydrocarbon fuel, such as gasoline, and air and injecting them into one or more cylinders of a conventional internal combustion engine. The pistons in the cylinders are permitted to compress the mixture of air and fuel. The amount of air mixed with the hydrocarbon fuel in a fuel rich carburetor is only sufficient to cause a partial oxidation of the fuel so that when the compressed mixture is ignited by a spark, it will not decompose, but rather is only partially oxidized to provide hydrogen

and carbon monoxide principally. The resulting gas mixture, termed a hydrogen rich gas, is then mixed with air and injected into the remaining cylinders of the internal combustion engine to be ignited by the spark plugs and is used in the well known manner of fuel to power the engine. The engine is run lean and the lean carburetor may be fed gasoline when more power is required. (See Houseman 1910 at Column 2, lines 34-68.) Houseman shows a conventional engine where the realistic rich limit is about 9:1.

The present engines are configured to produce a hydrogen rich exhaust and contemplate continuous production and dramatically different rich limits much beyond Houseman in hydrogen level of exhaust. The level of rich as achieved by the instant disclosure would cause rough running in the engine of Houseman. Normally, combustion near the rich limit of an internal combustion engine is very slow. The instant rich engine configurations with oxygen enrichment and/or rich homogeneous charge compression ignition, etc., enable combustion to be acceptably fast at much richer conditions than would otherwise be possible.

A recent SAE paper (SAE Paper No. 2004-01-0621) entitled "Partial Oxidation of Natural Gas Using Internal Combustion Engines" notes the difficulty with combustion beyond 30% combined carbon monoxide and hydrogen. A copy of this paper is attached herewith as Appendix A. A combined concentration of 30% carbon monoxide and hydrogen is not achievable with a conventional engine. One must do what the present inventors have done employing a rich engine configured to get beyond 30% (such as with HCCI, pre-reformer, oxygen enrichment, etc.).

Further, the present engines separate the production and use of the hydrogen rich exhaust by providing a first device, the engine, which is configured to produce the hydrogen rich exhaust which can then be used as fuel to feed a second separate device (i.e., the energy conversion device such as a fuel cell, etc.). The instant invention eliminates the coupling of torque and speed found in Houseman. The present separate

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hydrogen generation makes the flow rate and concentration independent of the working device.



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**DOUBLE PATENTING REJECTION**

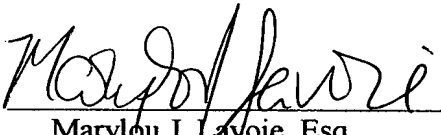
Applicants note that claims 17-33 of co-pending Application No. 10/387,663 were cancelled.

Based upon the remarks presented herein, the application has been placed in condition for allowance. As a result, Applicants respectfully request that a timely Notice of Allowance be issued in this case.

Should the Examiner have any questions regarding this matter, the Examiner is requested to contact Mr. Paul L. Marshall, who may be reached in the Troy, Michigan area at (248) 813-1240.

If there are any additional charges with respect to this Response or otherwise, please charge them to Deposit Account No. 50-0831 maintained by Applicants' attorney.

Respectfully submitted,  
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# Partial Oxidation of Natural Gas Using Internal Combustion Engines

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## ABSTRACT

Natural gas (methane) fueled engines are a new technology which can produce power as well as synthesis gas. The power from the engine is useful in a variety of direct drive systems, i.e. HVAC or stationary generators. However, its application should be limited to non-mobile applications because of the extra systems necessary to capture and separate the hydrogen. The hydrogen obtained from the system can then be used to power fuel cells for a direct electro-chemical process, or to enrich other fuels in other internal combustion engines. In this report, the operating conditions of the methane fueled modified compression ignition engine are subjected to some narrow band parametric investigation. The temperature and pressure distributions and species concentrations are reported. Engine performance data including air-fuel ratio, thermal efficiency, indicated specific fuel consumption and gross indicated power are calculated. The effects of intake temperature and equivalence ratio on temperature and pressure distributions and species concentrations are studied. The chemical kinetics approach is used in the model to numerically simulate the combustion of natural gas in the engine. All the stages of combustion including the initial non-equilibrium one are captured. For this analysis, a chemical kinetic code, CHEMKIN 3.71 is used.

## INTRODUCTION

Generally Partial Oxidation or Gasification in power generation applications consists of converting a fuel that is often "dirty" (such as coal, refinery, residue and biomass) and cannot be directly used in an engine or a fuel cell, to a clean gaseous fuel, which meets the engine specifications as well as the environmental emission standards. The natural gas is considered as a raw material for producing many chemical products and fuel. Fortunately, the reserves of natural gas (mainly methane) are available and continue to increase worldwide. Also, synthesis gas, CO and  $H_2$  is used as a feedstock for methanol, gasoline and other fuels. One way to produce syngas from natural gas is the use of the partial oxidation of methane (and other hydrocarbons) using an engine as a chemical compression reactor and power generator.

The use of internal combustion engines to produce syngas is feasible, and has been reported by several researchers, for example Karim and Moore (1, 2), Yamamoto, Kaneko, Kuwae and Hirastsuka (3), and Batenin et al (4). There are three ignition methods to initiate chemical reaction in natural gas engine; spark ignition (3), diesel pilot injection (1, 2), and homogeneous charge compression ignition (HCCI) (5).

Parameter	Value
Cylinders	1
Valves	4
Strokes	4
Bore	130 mm
Stroke	150 mm
Clearance Volume	153 cm <sup>3</sup>
RPM	1000
Compression Ratio	13
$L/L_a$	7
$P_{in}$	3.5 atm
Fuel	CH <sub>4</sub>

**Table 1: General Engine Operating Parameters**

HCCI is the auto-ignition of charge as a whole and it is the simplest solution. The lack of a spark plug and the need for low-pressure injection systems increases the durability of the engine. It has a short burning duration that increases the efficiency and average temperature of the reaction. The engine must tolerate the maximum cylinder pressure. HCCI produces very high rates of pressure, which produce noise. The phenomenon is auto-ignition and is controlled just by temperature; see work by Lawrence Livermore (LLNL) (5).

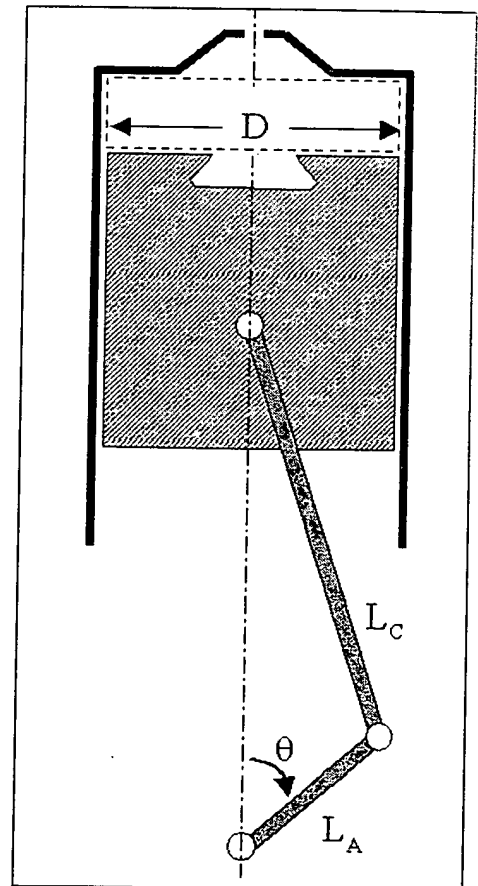
## CONFIGURATION – CONDITIONS

For this investigation, a modified turbo-charged compression ignition engine is modeled with the help of the CHEMKIN Aurora, perfectly stirred reactor model. The GRI-Mech 3.0 reaction mechanism and thermodynamic data were used to model the system. The reaction mechanism is a detailed methane air chemistry including 325 steps involving 53 species [6]. The Important Engine design parameters that are not varied are summarized in Table 1.

The CHEMKIN perfectly stirred reactor model, AURORA, has an internal combustion engine model. The AURORA software, can predict the time-dependent properties of a well-mixed reactor. An internal combustion engine-cylinder model is included in the AURORA application for modeling in this modified compression ignition engines. The internal combustion engine model is designed to model the chemical kinetics of a single cylinder compression ignition engine [7]. The cylinder model used by CHEMKIN is depicted in Figure 1. Throughout this analysis it should be kept in mind that only the compression and expansion strokes are considered by CHEMKIN. For some engine performance parameters this is important because one more pumping cycle is necessary to complete the system. The model is a single zone and the average pressure and temperature are calculated in the combustion chamber.

CHEMKIN Aurora utilizes a simple compression ignition engine model based on Heywood's book [8]. To use this model you must specify several engine parameters. For example, the gas intake temperature and pressure are specified in the aurora input file. Also some of the parameters that may not normally be set when operating a real engine are locked by CHEMKIN. The engine speed is a constant, continuous function of crank angle. Because of this, the engine is not allowed to speed up or slow down relative to the pressure inside the cylinder at any point.

Heat Transfer is included in some of these evaluations. The convective heat transfer from the combustion chamber is defined through the Nusselt number description. CHEMKIN assumes a Nusselt number of  $Nu_h = aRe^bPr^c$ . Where a, b, and c are specified by the user along with the cylinder diameter, and wall temperature. Values of a, b, and c were assumed based on Heywood's book [8] and were not varied for different cases. Irregardless of this, all cases were performed adiabatically as well in order to produce a reaction, where it was otherwise not possible, and to observe the general effect of heat transfer. The heat transfer condition,(adiabatic or convection) was held constant in all comparisons, unless specifically mentioned.



**Figure 1: Cylinder Model from Chemkin**

## RESULTS

First, a slightly rich fuel-air mixture was used in the analysis. Also, a realistic gas mixture temperature is assumed for gasses leaving a turbocharger. The fuel-air equivalence ratio ( $\phi$ ) is set to  $\phi=1.25$ , the gas inlet temperature is set

to  $T=500\text{K}$ , and all other parameters are held constant per. Heat transfer is considered *only* in this part and not in the other sections.

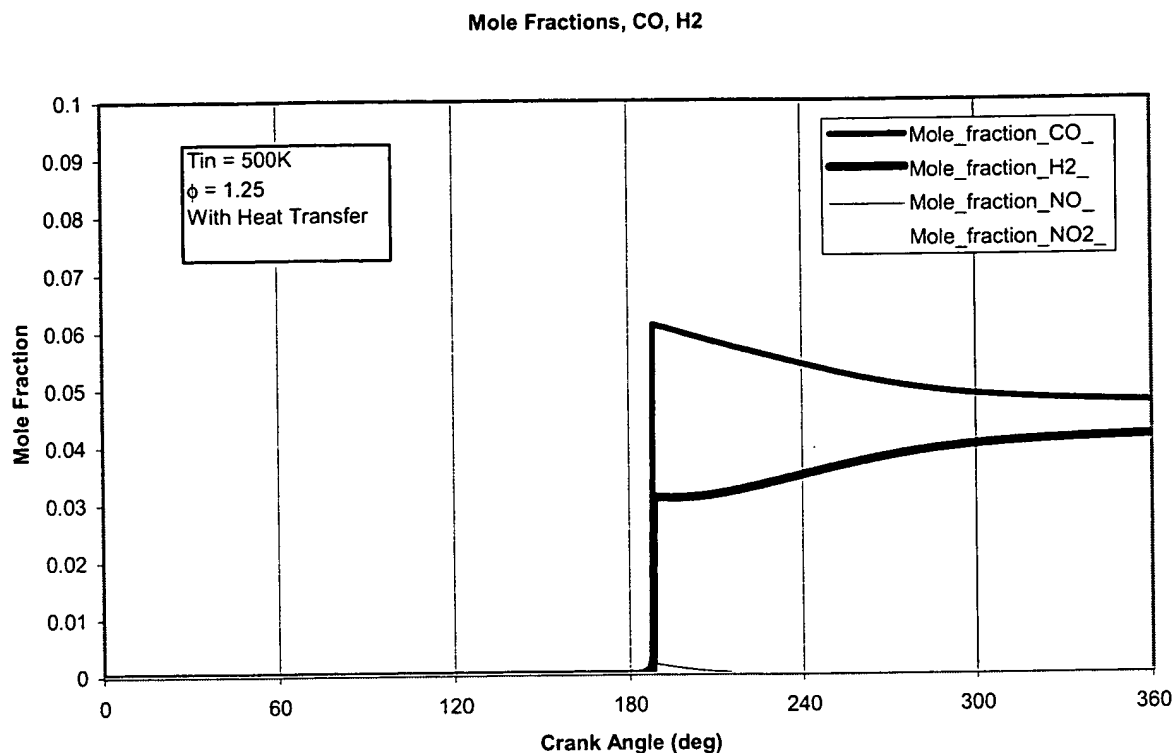


Figure 2: Species Concentrations (Mole Fractions) of CO, H<sub>2</sub>, NO, and NO<sub>2</sub> throughout the compression and Expansion strokes. (BDC = 0°, 360°; TDC = 180°)

The molar concentrations as a function of crank angle are shown in Figure 2. Only the mole fractions of H<sub>2</sub>, CO, NO, and NO<sub>2</sub> are shown. H<sub>2</sub> and CO are the interesting species at the end of the cycle. The other species have nearly vanished, in the case of NO<sub>2</sub> or CH<sub>4</sub>, or are nearly at their beginning concentrations, i.e. N<sub>2</sub>. It can be seen from the plot that there is more CO than H<sub>2</sub> at the end of the process. All other species are negligible, based on the fact that we are interested in harvesting the H<sub>2</sub> for other processes. The CO a pollutant gas that must be minimized. This result is undesirable because we are producing more CO than H<sub>2</sub>.

Figure 3 shows the volume, pressure and temperature as a function of crank angle for

this compression ignition engine case. The pressure and temperature increase correspondingly to the decrease in volume. The pressure increases by several orders of magnitude, while the temperature only increases by a couple hundred K, until starting of chemical reaction. Combustion occurs slightly after the peak temperature/pressure due to compression. This is because of the ignition delay, which may be a result of heat loss to the cylinder wall.

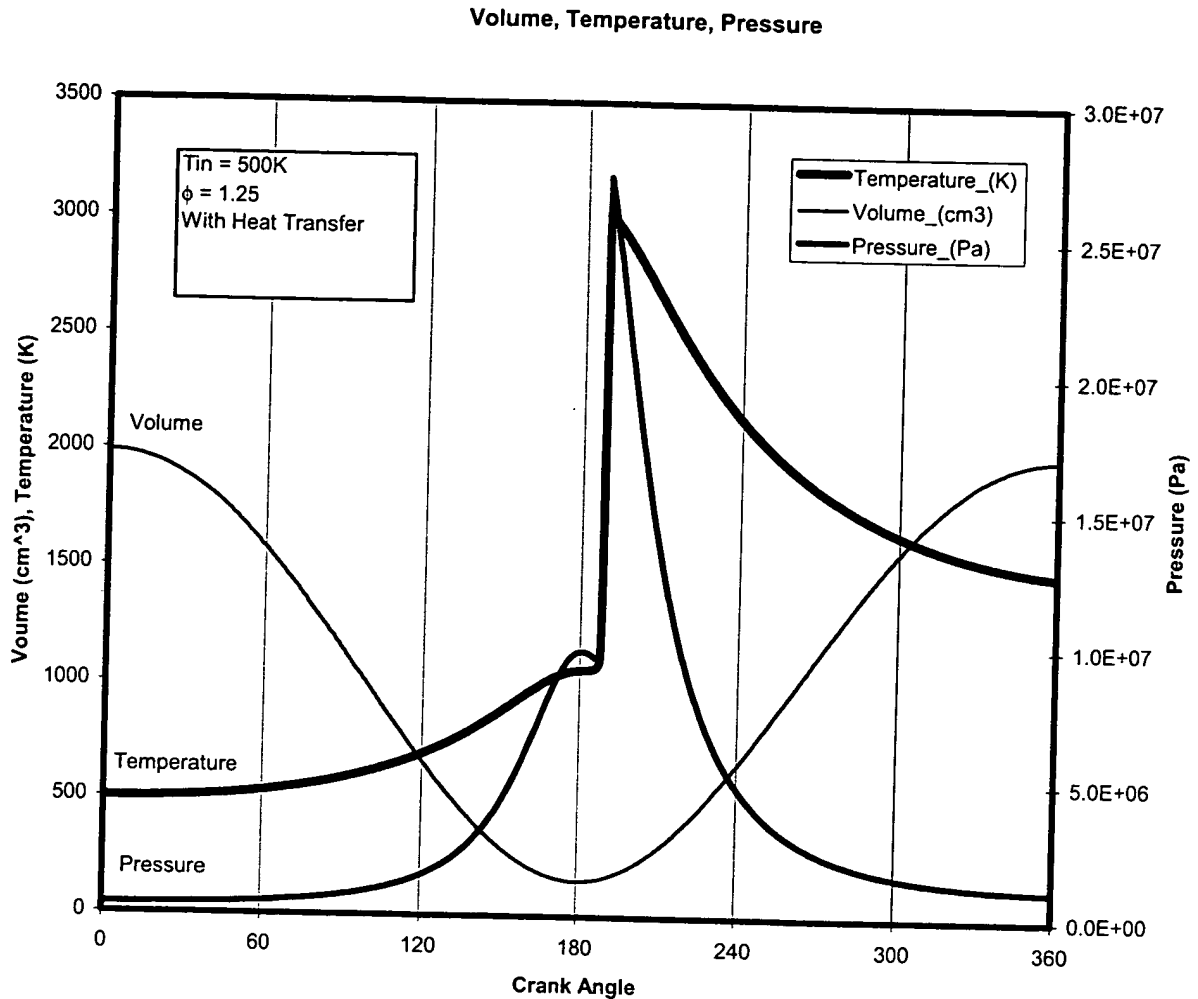
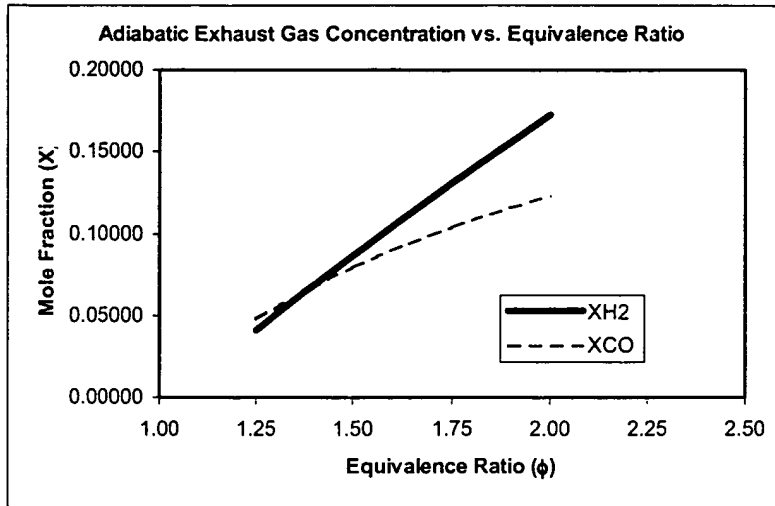


Figure 3: Volume, Temperature, and Pressure of compression and expansion strokes.

Now, the equivalence ratio will be varied throughout a range and all other parameters will be held constant. The equivalence ratio will be increased in increments of  $\phi=0.25$  until no more reaction is observed.

The exhaust species concentrations for the different cases are listed in Table 2. The trend in the change of concentrations with equivalence ratio is shown in Figure 4. A detailed graph of the crank angle progression of these important exhaust species is included in Appendix. The amount of each of these components in the exhaust gas increases with equivalence ratio. It should also be noted that the dominate exhaust species changes from CO to  $H_2$  at some point

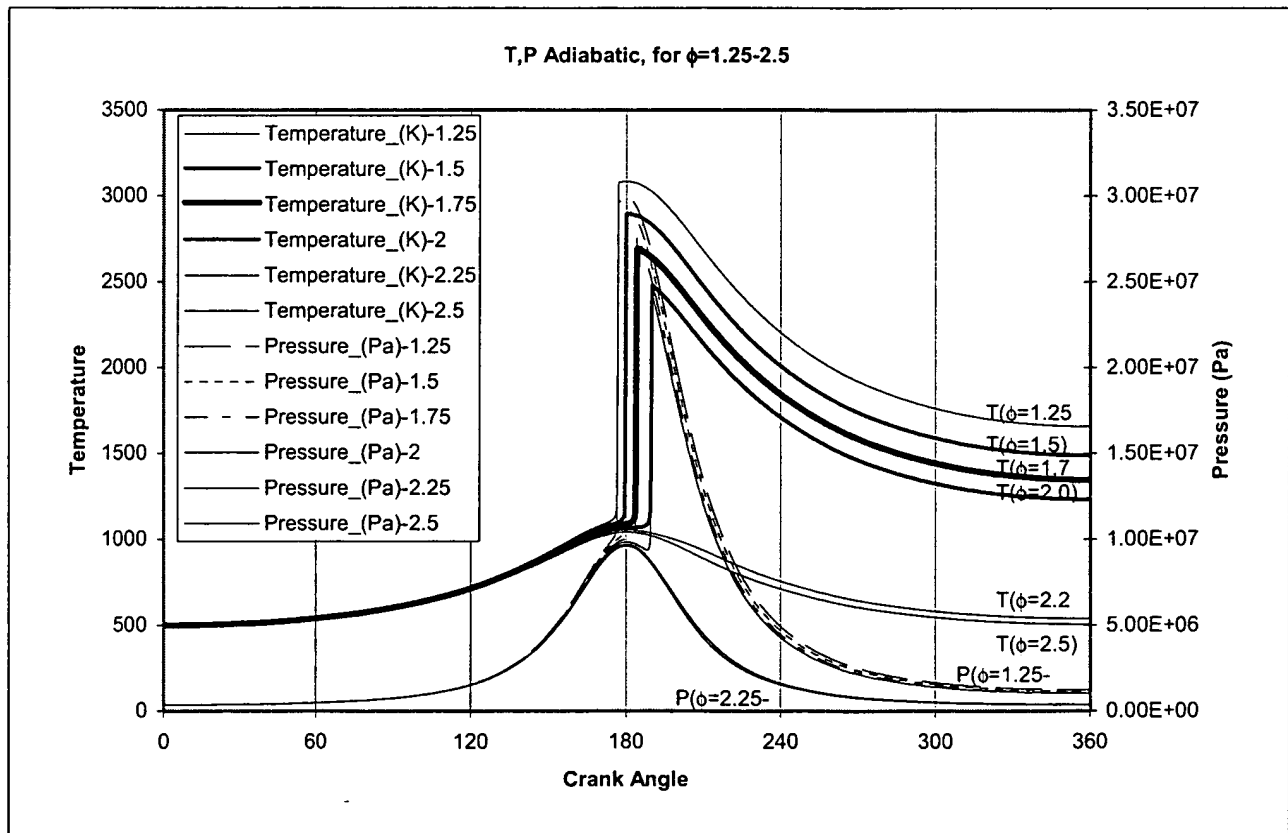
between  $\phi=1.25$  and  $\phi=1.5$ . Increments of 0.25 were used so there is not enough resolution to say exactly where this crossing occurs. Figure 5 shows the variation of temperature and pressure of the system under different equivalence ratios. The highest temperatures and pressures occur at  $\phi=1.25$ . This makes sense because we would expect less energy to be released at higher equivalence ratios. We can anticipate this because the amount of oxidizer available to convert the fuel to products decreases. The variation of temperature is linear with equivalence ratio, however the variation of pressure is curved.



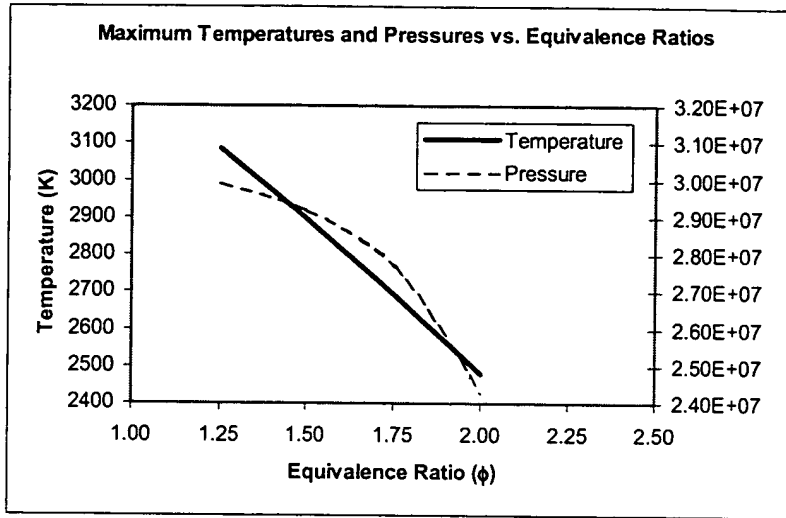
$\phi$	$X_{H_2}$	$X_{CO}$
1.25	0.04074	0.04789
1.50	0.08662	0.07964
1.75	0.13098	0.10375
2.00	0.17291	0.12270
2.25	0.00014	0.00000
2.50	0.00001	0.00000

**Figure 4: Exhaust Gas Species Concentration vs. Equivalence Ratio**

**Table 2: Exhaust gas Concentrations**



**Figure 5: Temperature and Pressure vs. Crank Angle for  $\phi=1.25-2.5$**



$\phi$	Temperature	Pressure
1.25	3083.716	29900430
1.50	2895.775	29172880
1.75	2691.629	27677930
2.00	2479.289	24295830
2.25	1053.329	9711104
2.50	1041.386	9601835

**Figure 6: Maximum Temperatures and Pressures as a function of Equivalence Ratio**

**Table 3: Maximum values of Temperature and Pressure**

The effects of inlet temperature are investigated at a constant equivalence ratio of 1.75. First, the gas inlet temperature is set to 475K. However, it was found that no combustion occurred at an inlet temperature of 475K. An incremental increase ( $\Delta T = 5K$ ) of the inlet gas temperature was made until combustion was found to occur. All cases were considered as adiabatic systems. Combustion was found to occur at an inlet temperature of 485K. Under different inlet temperatures, the engine behaves differently. Figure 7 shows a comparison of the pressure and temperature traces of simulated combustion processes with starting inlet temperatures of 485K and 500K.

It can be seen from this figure that the maximum temperatures and pressures of the system are higher for the case where the inlet temperature was set to 500K. A simple look at the maximum values of the temperature and pressure, Table 4, shows that the maximum temperature in the

cycle only increases by the same fraction as the inlet temperature, ~3%. However, the maximum pressure increases by a much larger amount, ~24%, between the two inlet temperatures. This shows that the effect of inlet temperature mainly influences the pressure, and has less effect on the temperature of the system. It is interesting to note that when the work output is calculated, this only results in a 5% increase in power. Note that even if the maximum pressure is increased substantially, it is the power that is important. This dramatic increase in maximum cycle pressure is due to the point at which combustion starts. The hotter gas ( $T_{in}=500K$ ) starts burning earlier, closer to top dead center. Because of this the nominal cylinder pressure due to pumping is maximum when the heat of combustion is also increasing the pressure. Therefore the largest influence is in the location of ignition start (or the length of ignition delay).

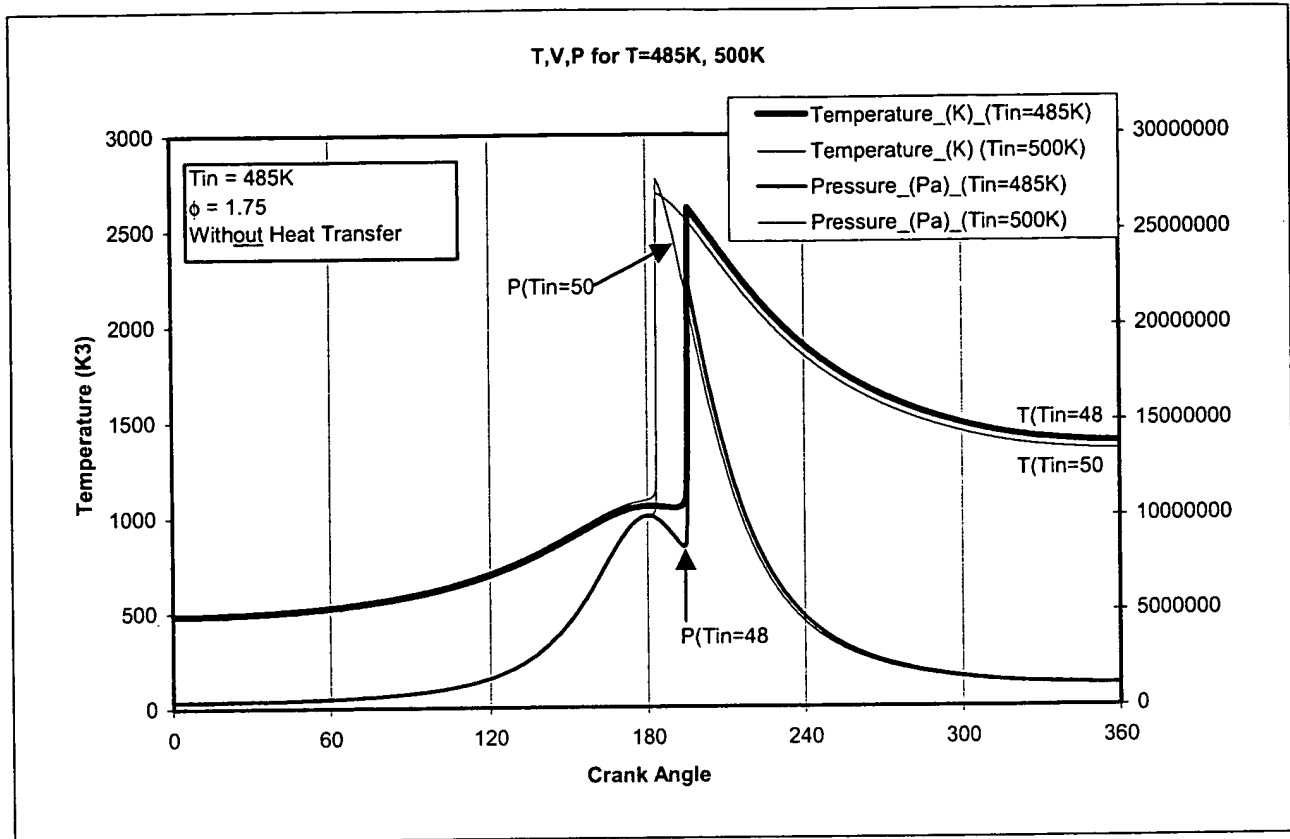


Figure 7: Temperature, Pressure, and Volume vs. crank angle for inlet conditions  $\phi=1.75$  and  $T=475K$

	T	Max T	Max P
Val 1	485	2614.913K	2.23E+07Pa
Val 2	500	2691.629K	2.77E+07Pa
Difference	15	76.716	5.40E+06
% Below Val 2	3.00%	2.85%	19.51%
% Above Val 1	3.09%	2.93%	24.25%

Table 4: Maximum Temperature and Pressure values comparing inlet temperatures of 485K and 500K

## CONCLUSIONS

A methane powered modified compression ignition engine is investigated to observe how varying various inlet parameters will affect exhaust species and engine performance. In order to encompass the largest variety of planned inlet conditions most systems were taken as adiabatic because ignition may fail to occur due to heat loss. Adiabatic results are compared with adiabatic results, to maintain

consistency. It was shown that as the equivalence ratio is increased the ratio of  $H_2$  to CO in the exhaust stream increases. Since the higher ratio of  $H_2/CO$  is desired, from crossing the  $H_2$  and CO, it is found that the relative equivalence ratio must be more than 1.4. Additionally the performance of the engine through different inlet equivalence ratios was investigated. It was found that in the range of



$\phi=1.25 - 2.5$  the efficiency, first, increases from  $\phi=1.25 - 1.5$ . This is due to the fact that the starting of pressure rise at  $\phi=1.25$  occurs slightly before top dead center. Then, after  $\phi=1.5$ , indicated efficiency drops off to essentially zero for the higher ratios where no combustion reaction occurs. It is concluded that the control of the reaction at different operating conditions is very difficult. The "trigger" inlet temperature and consequently the temperature of auto-ignition need to be adjusted such that it provides maximum pressure slightly after top dead

center. If the combustion occurs too early, the pressure rise before top dead center can cause severe damage. The maximum temperatures and pressures of the cycle are also steadily decreasing as the equivalence ratio is steadily increased. This may be acceptable, however, while the exhaust  $H_2$  concentration increases drastically as the efficiency goes down. This is illustrated in Figure 8. The influence of equivalence ratio on the performance and exhaust of the engine is shown to be very strong.

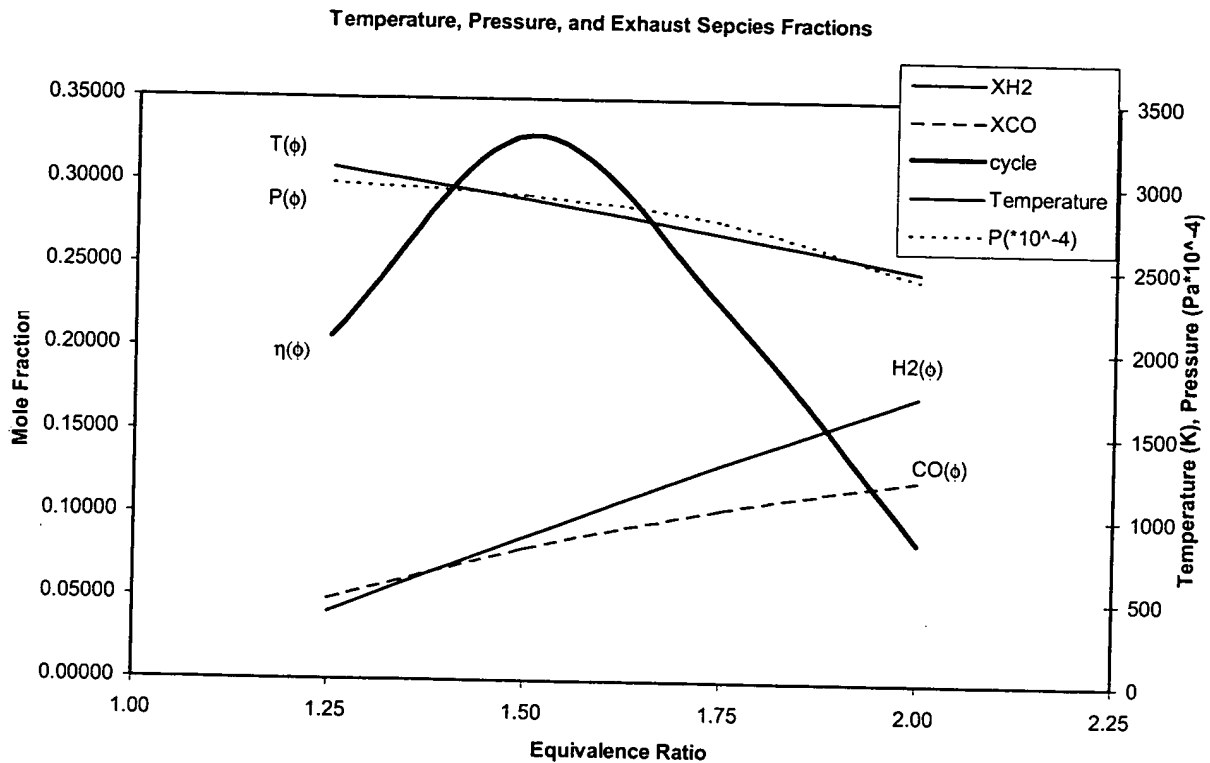


Figure 8: Temperature, Pressure, Exhaust Species, and Efficiency as a function of Equivalence Ratio

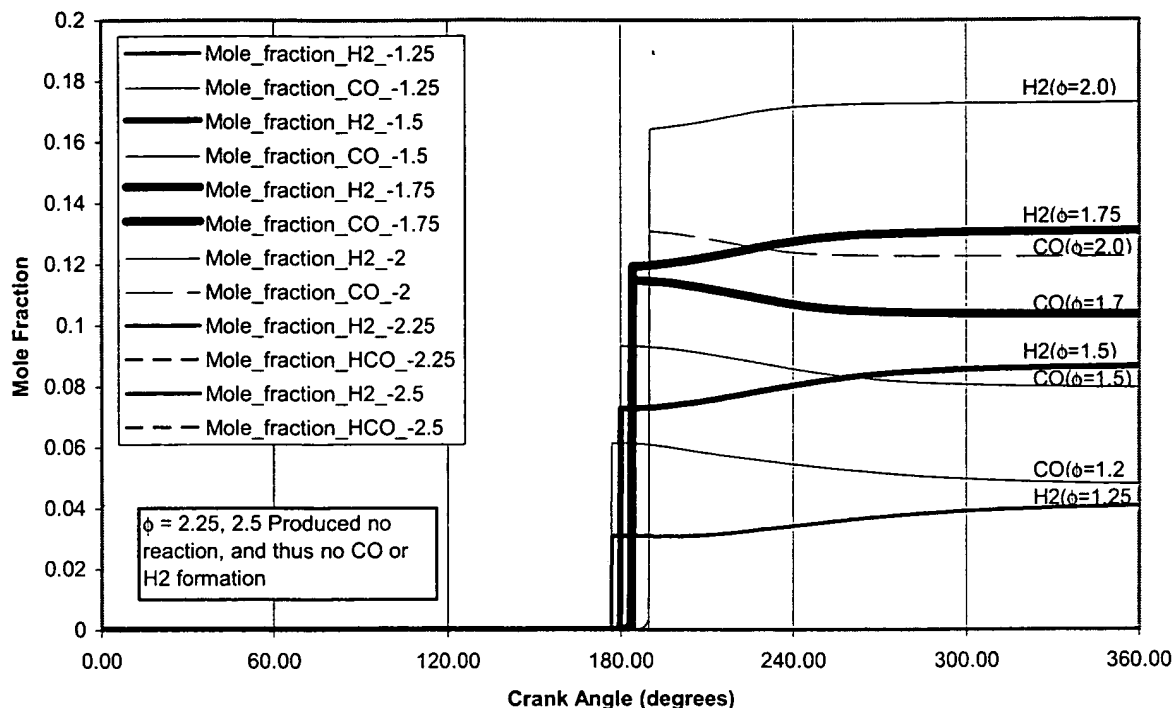
The influence of temperature is less dramatic than that of equivalence ratio. The change in the outlet composition fractions is very small (~0.1%) so it is not shown here. The change in the maximum temperature and total work is also relatively small (~5%). The most dramatic

change with temperature is the maximum cycle temperature. This result is due to the ignition delay and the difference in when the combustion starts and ends relative to the piston position. Therefore the inlet temperature mainly influences the ignition start time.

## Appendix

H<sub>2</sub>( $\phi=2.0$ )

### H<sub>2</sub> and CO Concentrations



Time evolution of H<sub>2</sub> and CO concentrations in exhaust gas from the methane fueled compression ignition engine, adiabatic conditions.

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